

## DISTRIBUTION AND GENETIC SIGNIFICANCE OF ALUMINIUM HYDRATES IN SOUTH-EAST JOHORE, MALAYA

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### Abstract

All three aluminium hydrate minerals—gibbsite, boehmite, and diasporc—are to be found in the laterites and bauxites of SE. Johore. However, two of these, gibbsite and boehmite, are confined to Recent bauxite, whereas diasporc occurs only in Tertiary laterites.

In contrast to the characteristically tough indurated diasporc-pyrophyllite-kaolinite-quartz Tertiary laterites, the Recent Johore bauxites constitute characteristically earthy red residual horizons flanked by some reworked colluvial horizons. Examination of the 'clay' and concretionary fractions of the Recent bauxites shows that whereas the concretionary fractions are mainly constituted of gibbsite, the 'clay' fraction comprises kaolinite, boehmite, gibbsite, halloysite, and goethite. This differential segregation of gibbsite and boehmite in clay and concretionary fractions respectively is also found to pertain in some Australian deposits—notably at Weipa, Gove, and in the Darling Ranges. Furthermore, the proportional increase in boehmite relative to gibbsite with depth is also shared in earthy bauxite horizons of Gippsland, the Darling Ranges and, to a lesser extent, at Gove.

In accordance with some experimental work but in direct contradiction to the majority of field interpretations, it is considered that probably the earliest aluminium hydrate to form was boehmite and that, with increasing maturity, this was progressively replaced by gibbsite, although some boehmite may form together with kaolinite under extreme desiccation of a gibbsitic bauxite horizon. Diasporc, on the other hand, appears to be an exclusively late-stage aluminium hydrate and is here essentially metamorphic in origin.

### Introduction

The Johore bauxite deposits, situated on the south-eastern tip of the Malayan peninsula, are both residual in nature and Quaternary in age. But in contrast to their abundance in Australia, Tertiary laterites are represented only by a few relict cappings of diasporc-bearing rocks on Bukit Pengerang, Batu Mas, and China; these in turn being overlain by derived Quaternary bauxites.

Within the upper levels of the recent bauxite horizons (Grubb 1962, 1963) the ore becomes coarsely concretionary with incipient formation of the Australian-type duricrust or hard-cap. Large irregular limonitic concretions occur throughout these sections and frequently account for a considerable downgrading of the ore. Furthermore, derived colluvial bauxite horizons are distributed widely over the flat southern plain flanking these deposits but, being essentially composed of gibbsite and kaolinite, are of little mineralogical interest.

The predominant earthy red residual bauxite comprises concretionary and clay fractions in varying proportions. The concretionary bodies range in size from less than 1 mm to over two metres in width. In shape also they include oolites, irregular nodules and concretions, shale-like forms, and 'stick' bauxite (Pl. 30B). However, the typical zoned pisolites of Australian bauxites are entirely lacking in Malaya.

### Microscopy

Owing to their predominantly cryptocrystalline texture, microscopic examination of Recent Johore bauxites is of limited value, although some very weak zoning in

concretions may occasionally be seen together with relict textures of the bauxitized rhyolites, granophyres, and granites. On the other hand, due to their more indurated nature, thin sections are readily obtained from the Tertiary diasporic laterites. In these, diasporic is conspicuously porphyroblastic with sub- to euhedral crystals up to 0.7 mm long enclosed in a fine-grained matrix of pyrophyllite, kaolinitic, and quartz (Pl. 30A). Accessory constituents include magnetite, cassiterite, and allanite. In the most siliceous laterites diasporic is generally separated from the predominant quartzose matrix by a thin envelope of pyrophyllite. Sometimes, too, both diasporic and pyrophyllite may be observed lining what appear to be minute drusy cavities.

Polished surfaces from the large limonitic concretions associated with the earthy Quaternary bauxites reveal a conspicuous colloform texture with successive bands enclosing porous cavities, gibbsitic patches, or relict quartz grains. The predominant mineral present is poorly crystalline goethite, this being almost amorphous in character adjacent to the cavities. Scattered throughout, however, are small anhedral steelish-grey maghemite crystals together with some yellowish-grey manganiferous magnetite. Although X-ray diffraction patterns indicate the presence of some lepidocrocite, this was not positively identified microscopically.

TABLE 1

## A. Chemical analyses of concretionary and clay fractions from bauxites in SE. Johore

	1	2	3	4	5	6	7	8
Loss on ignition	20.00	30.80	22.87	29.67	31.60	33.30	13.45	13.20
SiO <sub>2</sub>	22.20	5.20	25.68	7.52	6.76	1.91	3.25	2.42
Fe <sub>2</sub> O <sub>3</sub>	11.60	3.64	11.52	4.56	3.25	2.54	53.40	59.65
TiO <sub>2</sub>	0.40	0.20	1.02	0.49	0.30	0.30	0.60	0.80
Al <sub>2</sub> O <sub>3</sub>	46.80	60.70	38.91	57.76	57.80	62.30	30.60	23.75
MnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.18
Total	101.00	100.54	100.00	100.00	99.71	100.45	101.30	100.00

Analysts: T. H. Donnelly &amp; N. Philip

## B. Estimated approximate modal analyses based on X-ray diffraction, infrared absorption, and thermogravimetric analyses plus computations based on chemical analyses

	1	2
Quartz	9.5	nil
Opaline silica (SiO <sub>2</sub> .H <sub>2</sub> O)	6.8	2.4
Gibbsite (crystalline)	28.0	44.0
Gibbsite (amorphous)	5.0	38.0
Boehmite (amorphous)	22.0	8.0
Goethite (crystalline & amorphous)	13.0	4.0
Kaolinite (crystalline)	16.0	7.0
Anatase (amorphous)	0.4	0.2
Total	100.70	103.6

- 1 —300 mesh (B.S.S.) clay fraction from the earthy red bauxite of Bukit Tanah Merah.
- 2 Nodular  $\frac{1}{4}$ " to  $\frac{1}{2}$ " fraction of the earthy red bauxite (1).
- 3 —300 mesh (B.S.S.) clay fraction from the earthy red bauxite of Bukit Simon.
- 4 Concretionary fraction from the same sample as (3).
- 5 Shaly 1" to  $\frac{1}{2}$ " fraction from the earthy red bauxite of Bukit Tanah Merah.

- 6 Coarse +1" concretion from the earthy red bauxite of Bukit Tanah Merah.  
 7 Black limonitic layer concretion from the earthy red bauxite of Bukit Tanah Merah.  
 8 Black limonitic concretion from the earthy red bauxite of Bukit Simon.

### X-ray diffraction

Qualitative and quantitative X-ray diffraction analyses of composite earthy bauxite samples from two localities (Bukits Tanah Merah & Simon) in south-east Johore show that, whereas in exceptional conditions up to 11% boehmite may occur in the concretionary fraction, this constituent is almost exclusively confined to the fine clay fraction. Approximate modal analyses of these two fractions, as determined by combined X-ray diffraction-, infrared-, chemical-, and thermogravimetric analyses, are shown in Table 1.

Apart from some possible residual forms in the Pengerang area, diaspore has not been detected in any of the Quaternary bauxites of Johore. Yet, in the Tertiary laterites on Bukits Batu Mas and Pengerang, it forms conspicuous sub- to euhedral crystals up to 2 mm long embedded in a finer matrix of quartz pyrophyllite and kaolinite. The X-ray diffraction data, unit cell parameters, and optical properties of this diaspore are listed in Table 2.

TABLE 2

#### A. X-ray diffraction data for diaspore from SE. Johore

<i>hkl</i>	<i>d A (meas.)</i>	<i>d A (calc.)</i>	<i>I</i>
020	4.72	4.70	10
110	3.98	3.98	100
120	3.213	3.209	10
130	2.551	2.551	40
021	2.419	2.431	5
040	2.348	2.351	10
111	2.312	2.311	60
121	2.124	2.126	50
140	2.071	2.073	50
131	1.895	1.898	2
041	1.810	1.811	5
211	1.708	1.708	20
221	1.628	1.629	50
240	1.603	1.604	20
060	1.566	1.568	5
231	1.517	1.521	10
160, 151	1.475	1.476	25
250	1.427	1.428	10
002	1.417	1.419	15
320	1.394	1.397	10
061	1.370	1.370	20
112	1.335	1.336	10
330	1.324	1.325	10
301	1.299	1.300	5
311, 170	1.283	1.290	10
251	1.273	1.276	2
321	1.254	1.253	7
340, 132	1.240	1.241	8
042	1.215	1.215	3
331	1.203	1.202	6
142	1.171	1.171	9
341	1.138	1.138	2
400	1.097	1.097	1
410	1.090	1.090	3

## Calculated unit cell data

$$a_0 = 4.38 \text{ \AA}$$

$$b_0 = 9.42 \text{ \AA}$$

$$c_0 = 2.83 \text{ \AA}$$

$$\text{Volume} = 116.7 \text{ \AA}^3$$

$$a_0 : b_0 : c_0 = 0.465 : 1 : 0.301$$

Fe/Mn radiation

Camera diameter 114.6

*B. Optical properties of diaspora from SE. Johore*Refractive indices:  $\alpha$   $1.696 \pm 0.004$  $\beta$   $1.708 \pm 0.002$  $\gamma$   $1.732 \pm 0.003$ Optical axial angle (2V) :  $86^\circ \pm 1^\circ$ 

Optic sign : Positive

 $\gamma - \alpha$  : 0.035

Elongation : Positive or negative

Cleavage : Perfect parallel to (010)

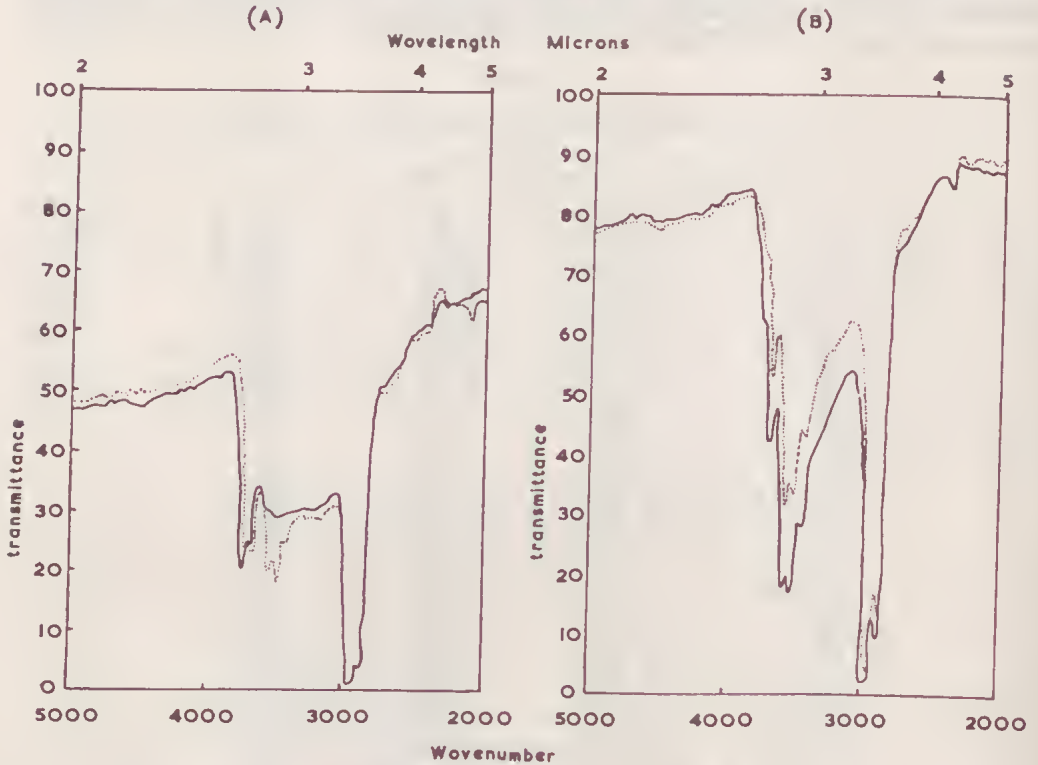


FIG. 1 — INFRARED ABSORPTION SPECTRA OF BAUXITE FROM SE. JOHORE.

(A) 300 mesh (B.S.S.) clayey fraction.

(B)  $\frac{1}{4}$  -  $\frac{1}{2}$  nodular concretionary fraction.

..... sample air dried only.

— sample heated at  $160^\circ\text{C}$  for 24 hours.**Infrared absorption spectra**

Although, in both the concretionary and clay fractions of the earthy Quaternary bauxite, infrared spectra reveal strong absorption bands characteristic of kaolinite

and gibbsite (with to a lesser extent quartz and opaline silica), yet only in the —300 mesh (B.S.S.) clay fraction were any weak bands identifiable with boehmite detected. Examination of infrared spectra (together with thermogravimetric and X-ray diffraction analyses) from these samples after heating at 160°C for 24 hours, however, revealed a conspicuous increase in boehmite and kaolinite with a corresponding decrease in the total gibbsite content (Fig. 1, 2, 3). From this it is assumed that, although some boehmite and kaolinite may originate by direct replacement of gibbsite, much in fact also formed by crystallization of the amorphous material—especially in the clay fraction.

### Thermal analyses

In further investigations into the clay and concretionary fractions of the earthy Quaternary bauxite, both were subjected to differential thermal and thermogravimetric analyses. The results were again of limited value for natural bauxite mineral associations—even with proportional plots—goethite being inseparable from gibbsite, and boehmite from kaolinite (Fig. 2, 3). Nevertheless, as the total iron content of these fractions is almost exclusively present in the form of goethite (or its gel form), these analyses are of some use when used in conjunction with chemical, X-ray, and infrared techniques.

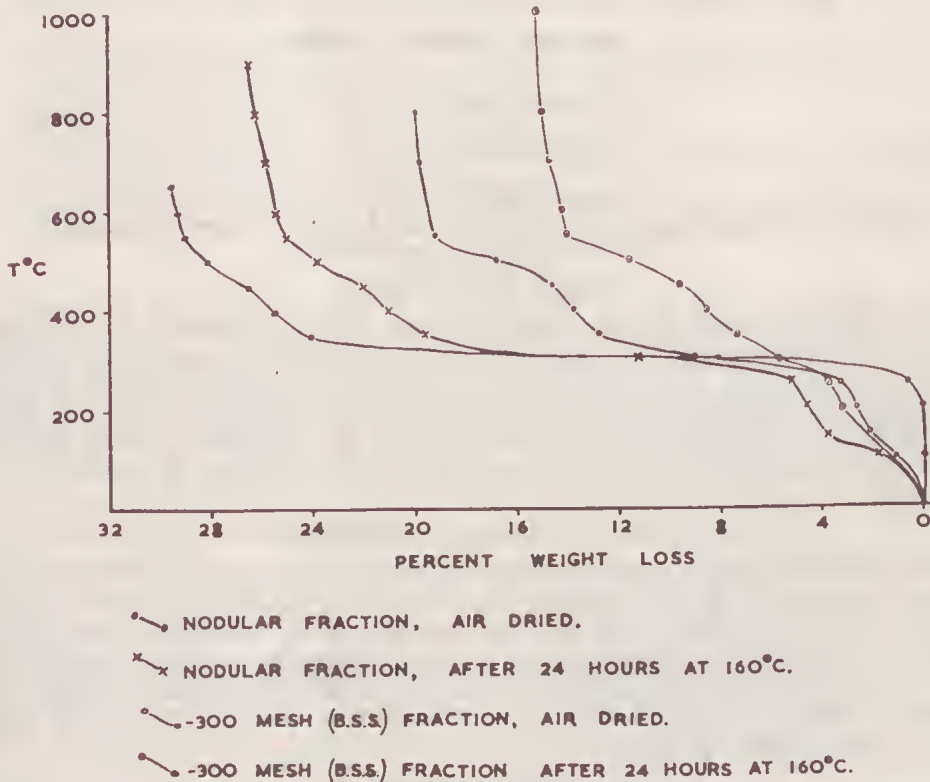


FIG. 2—Thermogravimetric analyses of  $\frac{1}{4}$ "– $\frac{1}{2}$ " nodular and —300 mesh (B.S.S.) 'clay' fractions from a typical earthy SE. Johore bauxite showing the effects of preliminary drying.

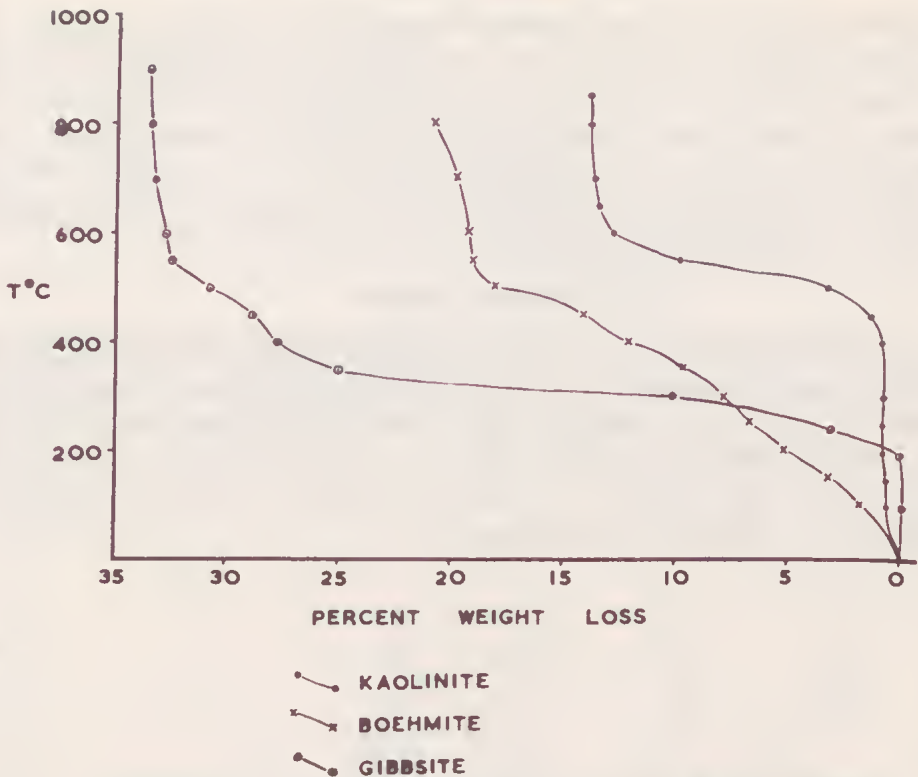


FIG. 3—Thermogravimetric analyses of the chief bauxite mineral components: kaolinite, boehmite, and gibbsite.

#### Heavy mineral study

In order to determine the insoluble heavy mineral content of the earthy Quaternary bauxites, and at the same time to confirm the absence of any diaspore in these, 50 gm from two such samples were leached in warm sulphuric acid and the residue centrifuged in bromoform. Concentrates of only 0.010% and 0.002% were obtained, these containing variable amounts of tetrahedrite, zircon, goethite, chalcopyrite, anatase (leucosene), and magnetite. However, no diaspore was detected.

#### Electron microscopy and diffraction

Electron diffraction patterns of film suspensions from the clay fraction of the Johore Quaternary bauxites reveal that, whereas regular hexagonal kaolinite platelets form the predominant clay constituent, a little halloysite is also present while, in addition, non-diffracting amorphous gel particles are common (Pl. 31). Further, as in Darling Ranges, earthy bauxite horizons, boehmite crystallites are seldom discernible—a factor which would account for its characteristically broad basal X-ray diffraction peak.

#### Chemical analyses

Chemical analyses of the Tertiary diaspore laterites and fractions of the Quaternary bauxites are listed in Tables 1 & 3. Little compositional similarity

exists between the Tertiary laterites and Quaternary bauxites, although the former are far closer to the rhyolitic tuffs and lavas which form the parent rocks for both. Furthermore, in the Quaternary bauxites there is a general decrease in silica and  $\text{Fe}_2\text{O}_3$  contents from the fine clay to the coarser concretionary fractions (Table 1).

TABLE 3

*Chemical analyses of some diaspore-pyrophyllite hornfelses and acid volcanics from SE. Johore*

	1	2	3	4	5	6	7
$\text{SiO}_2$	81.90	54.20	77.30	69.05	67.75	45.00	13.78
$\text{Al}_2\text{O}_3$	15.50	34.75	12.31	13.90	21.30	32.50	44.34
$\text{Fe}_2\text{O}_3$	} 0.45	1.48	3.77	7.90	—	—	} 17.31
FeO				0.55			
MgO	n.d.	Trace	1.19	0.30	0.65	n.d.	—
CaO	n.d.	0.05	Trace	1.20	0.20	—	—
$\text{Na}_2\text{O}$	0.10	0.14	} 4.18	3.25	n.d.	n.d.	—
$\text{K}_2\text{O}$	0.14	0.20		3.25	n.d.	n.d.	—
$\text{Li}_2\text{O}$	0.06	0.08	} 2.79	n.d.	n.d.	n.d.	—
$\text{H}_2\text{O}^+$	2.15	7.93		nil	} 8.20	} 13.50	} 23.42
$\text{H}_2\text{O}^-$	nil	nil	nil	1.15			
$\text{TiO}_2$	0.45	0.25	0.22	0.37	0.35	1.00	
Total	100.75	99.08	100.00	99.77	100.00	100.00	100.00

- 1 Diaspore-pyrophyllite-kaolinite-quartz hornfels, Bukit Pengerang. Analyst: T. H. Donnelly.
- 2 Diaspore-pyrophyllite-kaolinite hornfels, Bukit Batu Mas. Analyst: T. H. Donnelly.
- 3 Fine banded ash-tuff, Bukit Panjang South. Analyst: P. L. C. Grubb.
- 4 Rhyolite, Johore. Municipal analyst, Singapore.
- 5 Kaolinized rhyolite, Johore. Municipal analyst, Singapore.
- 6 Average analysis of several kaolinitic clays underlying bauxites derived from andesite and rhyolite, Johore. Municipal analyst, Singapore.
- 7 Recent gibbsitic bauxite derived from Tertiary diaspore laterite on Bukit Batu Mas. Government analyst, Geological Survey H.Q., Ipoh.

### Conclusions

Owing to conflicting sources of evidence, the precise origin and nature of the chief aluminium hydrate minerals—gibbsite, boehmite, and diaspore—have remained something of a problem. The most widely accepted interpretation is that preliminary bauxitization gave rise to predominantly gibbsitic products which, with maturity and further desiccation of the surface horizons, were progressively replaced by boehmite (and, under certain peculiar conditions, diaspore). This hypothesis has been convincingly elucidated for the deposits at Weipa, N. Queensland (Loughnan & Bayliss 1961), while, at the same time, experimental confirmation of these processes was obtained by Pedro (1961). On this basis, too, it has long been assumed that bauxite deposits may be geographically subdivided into gibbsitic-, boehmitic-, and diasporic-varieties, with the first confined essentially to warm and moister equatorial regions and the diaspore and boehmite varieties to higher latitudes. However, recent detailed studies of bauxite profiles by the writer in Gippsland (Victoria), the Darling Ranges (Western Australia), and Gove (Northern Territory) have shown that some fundamental discrepancies in this theory exist. Thus, although a sharp increase in boehmite content with height in the bauxite profile is sometimes observed at Gove (N.T.) and in the Darling Ranges, in Gippsland the predominant trend follows a steady decrease.

As Australian bauxite deposits are essentially Tertiary in age, the occurrence of all three aluminium hydrate minerals in the Tertiary and Quaternary deposits of

south-east Johore, where bauxitization is also still in progress, seems to be of special genetic significance. Texturally and compositionally the nearest counterparts of the earthy Johore Quaternary bauxites are those of Gippsland (Victoria). Both, too, show a preferential concentration of boehmite in the fine clay fraction and a tendency for this constituent to increase relative to gibbsite with depth. From this the writer considers that bauxitization is generally initiated with hydrolysis of aluminosilicates in the parent rock to give complex gels, in which boehmite and gibbsite (in addition to goethite and opaline silica) are represented, occurring in almost equal parts. With ageing and a subsiding water table there followed a coagulation of gel particles with crystallization of gibbsite to form typical concretionary bodies. Thus, a differential segregation of gibbsite and boehmite in clay and concretionary fractions was initiated while, furthermore, as this process is strictly dependent on a falling water-table, a proportional increase in boehmite content with depth resulted.

In Gippsland, after a preliminary phase of bauxitization, the land surface appears to have subsided to be subjected to swamp conditions. With the consequent rapid rise in water table, the replacement of boehmite by gibbsite was arrested and the status quo maintained, this apparently explaining its similarity to the Quaternary bauxites of Johore.

Lateritic profiles showing secondary increases in boehmite content in their surface horizons (such as at Weipa and Gove), on the other hand, appear to derive in part from increased desiccation, this process being assisted by the more porous nature of these horizons and, at the same time, accounting for a corresponding increase in kaolinite. Alternatively, or in addition, this boehmite increase could be due to a corresponding rise in carbon dioxide content for, as Keith (1959) has shown experimentally, the transformation of boehmite to gibbsite can be arrested by saturation with carbon dioxide. Furthermore, excess carbon dioxide can independently result in a 30% increase in total evaporation rate (Sechrist 1963), which would clearly accelerate desiccation and, through induced upward capillary flow, result in increased surface precipitation of iron hydroxides in the form of a characteristic hardcap or duricrust horizon.

The paragenesis of diasporite is less clear than that of boehmite and gibbsite. Although associated with boehmite in several Tertiary bauxite deposits elsewhere, no boehmite was detected in the Johore Tertiary laterites. Furthermore, even in Australian deposits, only one rather doubtful occurrence of diasporite has been reported (Simpson 1951), although both diasporite and boehmite are associated in a kyanite schist at Thackaringa, N.S.W.

Although its lower stability limits are 275°C at 2,000 psi (Ervin & Osborn 1951, Roy & Osborn 1954), diasporite often occurs as late stage vein or cavity fillings (Allen 1952). Thus, as pointed out by these authors, a wide degree of metastability exists between the three aluminium hydrate minerals. Allen (1952) considers that their paragenesis is governed mainly by ageing but, at the same time, has suggested that, as boehmite and diasporite are commonly associated with flint clays, the characteristically disordered state of kaolinite could be an added factor.

Following the experimental work of Roy & Osborn (1954), it was found that diasporite can coexist in equilibrium with kaolinite and pyrophyllite at temperatures above 280°C. It seems unavoidable, therefore, especially in view of the characteristically indurated nature of the Tertiary diasporite laterites, that these are essentially metamorphic in origin, being derived by a rise in isotherms culminating in a



partial breakdown in the poorly crystalline kaolinite to form diaspore, pyrophyllite (and quartz).

In conclusion, therefore, it appears that, whereas gibbsite and boehmite represent typical lateritic products, known occurrences of diaspore both in Malaya (and Australia) by contrast are essentially of metamorphic origin.

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#### Explanation of Plates

##### PLATE 30

- A—Needles of diaspore in pyrophyllite from the Tertiary laterite of Bukit Batu Mas. SE. Johore. Ordinary light.  $\times 55$  magnifications.
- B—'Stick'-bauxite concretions from the earthy red bauxite of Bukit Tanah Merah.

##### PLATE 31

- Electron micrograph of the fine clayey matrix to the earthy red bauxite from Bukit Tanah Merah, showing 'tubules' of halloysite and particles of isotropic gel.  $\times 20,000$  magnifications.